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Elastic properties of thin fcc films

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We report the results of molecular-dynamics simulations on oriented fcc thin films. For thin films of (001) orientation we found that independent of the potential, the intrinsic structural instability of these films governed their elastic properties. All of the in-plane elastic constants increase with decreasing film thickness for thin (111) films modeled with use of embedded-atom-method potentials, whereas (111) films modeled with use of a Lennard-Jones potential gave entirely opposite results.

The elastic and structural properties of unsupported thin films are important theoretical considerations relating to the issues of interfacial stability of substrate-overlayer systems and elastic properties of small-period superlattice structures. Each of these issues has been the focus of considerable experimental and theoretical study in recent years.[1-14] Cammarata and Sieradzki[13] presented a thermodynamic model which predicts that for very thin unsupported films and superlattices with semicoherent or incoherent interfaces, surface stresses act to significantly displace atoms from the equilibrium positions which they would normally occupy in the bulk solid. The alterations in the interatomic distance affect the elastic properties of nanoscale structures. Using a Volterra dislocation approach, this model was used to reevaluate the critical thickness dependence on misfit for epitaxy.[15] The results, when compared to previous theories, predict larger (smaller) critical thicknesses when the stress-free lattice parameter of the film is greater (less) than the lattice parameter of the substrate.

A heuristic atomistic interpretation of the thermodynamic model is as follows. The creation of a free surface from an infinite solid produces two sources of surface stress owing to different "relaxation" effects. One source of surface stress develops from the relaxation of the outer layers in response to the loss of neighbors at the surface. The exact nature of the relaxation will depend upon details pertaining to the crystallographic orientation of the surface formed. In addition to this effect, the atoms in the vicinity of the surface take account of missing neighbors by increasing the strength of their interactions with remaining neighbors. This bond order effect results in a compressive surface stress. Calculations using empirical embedded-atom-method (EAM) potentials which properly account for these effects yield compressive surface stresses for bcc and fcc metals.[16,17] Atoms interacting via pairwise potentials exhibit only the interplanar relaxation in response to the creation of a free surface and do so in a manner as to *increase* the interplanar spacing between the first and second layers.[18,19]

In this Rapid Communication we present results of molecular-dynamics simulations aimed at determining the elastic properties and structural stability of unsupported thin fcc films. Our results are in agreement with the predictions of the model of Cammarata and Sieradzki[13] for films of close-packed orientation. In order to appropriately separate out various effects relating to the elastic properties of the thin films, we report on results of simulations with use of both a pairwise Lennard-Jones (LJ) potential and an analytic form of an EAM potential developed by Johnson.[20]

Simulations were performed for thin layers with (001) and (111) orientations. The samples were formed by stacking together from 1 to 20 layers (each composed of from 32 to 1250 atoms) in an fcc arrangement. The samples were constrained to be periodic in the $(x\text{-}y)$ plane of the film at constant temperature and pressure using a Parrinello-Rahman Lagrangian.[21] The results were found to be independent of layer size for layers with more than 20 atoms. Newton's equations of motion were solved using a fifth order Gear predictor-corrector algorithm and all simulations were performed at 0 K. Calculations using the LJ potential were cutoff at a distance halfway between the third and fourth nearest neighbor unless otherwise

noted. The empirical EAM potential was fitted for Cu. The elastic moduli were determined by applying very small stresses in plane and measuring the corresponding strains.

The simulation results for Young's modulus E, Poisson's ratio ν_{xy} in the plane of the film, and alterations in the interatomic distance as a function of the film thickness are shown for the two orientations in Figs. 1 and 2. Values of the Young's modulus for the (001) and (111) orientations were determined by applying a uniaxial stress in the [100] and [1$\bar{1}$0] directions, respectively. The biaxial modulus Y was also determined by the application of an equiaxial stress and the corresponding strain measurement. We found that the simulation results for the biaxial modulus could be described by the simple relation from linear elasticity, $Y=E/(1-\nu_{xy})$ and similarly the shear modulus G was described by the relation $G=E/2(1+\nu_{xy})$.

Surprisingly, the results for the LJ(001) and the EAM(001) thin films are in qualitative agreement. As the number of layers in the film decreases, E decreases and ν_{xy} increases, with a concomitant sharp decrease of G. The extreme softening in the shear modulus with decreasing film thickness displayed by (001)-oriented films is the result of the intrinsic structural two-dimensional instability of the (001) fcc surface. Simulations of a (001) fcc monolayer using either of the interatomic potentials resulted in a spontaneous transformation of this plane to a (111) fcc plane. This phenomenon was further investigated by examining the structural stability of LJ and EAM(001) fcc thin films between two and six layers in thickness by applying a stress state corresponding to pure shear. Various cutoffs on the range of the LJ potential were also examined (from second out past the fifth nearest neighbor). We found that in all cases (001)-oriented fcc films undergo a bulk structural transformation to (111) fcc. The transformation is driven by the reduction in surface energy gained in going to a close-packed face. The results for the (111)-oriented films indicate qualitative differences in behavior for the two potentials examined. The EAM films showed increasing values for E, ν_{xy}, Y, and G with decreasing film thickness whereas the LJ films displayed entirely opposite behavior, as indicated in Fig. 2. We examined the stability under shear loading of the EAM and LJ(111) films and found them structurally stable. The in-plane surface strains which develop in the LJ films do so as a Poisson response to the relaxed film thickness. The outermost layer of a (111) LJ surface relaxes outwards while the rest of the layers relax inwards, as can be explained by simple bond-cutting models.[18,19,22] Since all but the outer layers relax inward toward the film center, a Poisson effect produces tensile strains in the (111) planes and this results in the lowering of the in-plane elastic constants owing to the anharmonicity of the potential. The elastic behavior of the EAM films is dominated by the noncentral portion of the potential and this results in the development of compressive surface stresses

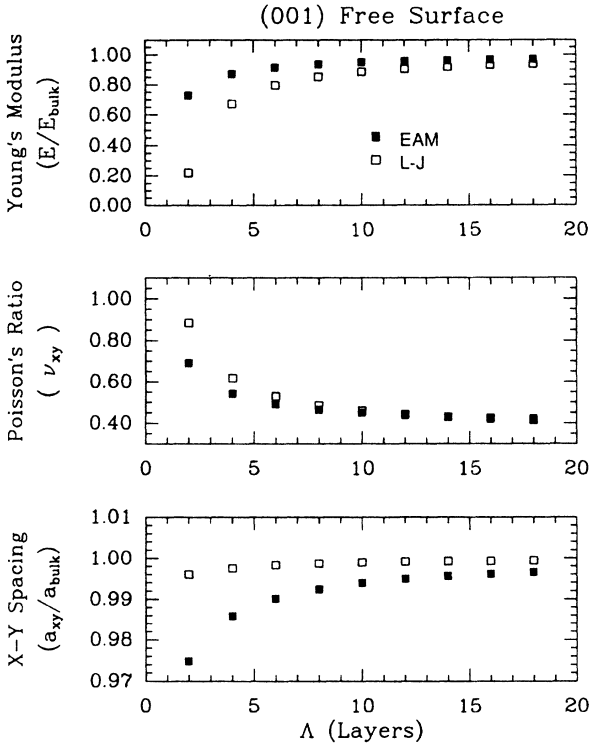

FIG. 1. Variation with film thickness of Young's modulus, Poisson's ratio, and lattice spacing in the plane for fcc films with a (001) orientation. The elastic constants have been normalized by their bulk values.

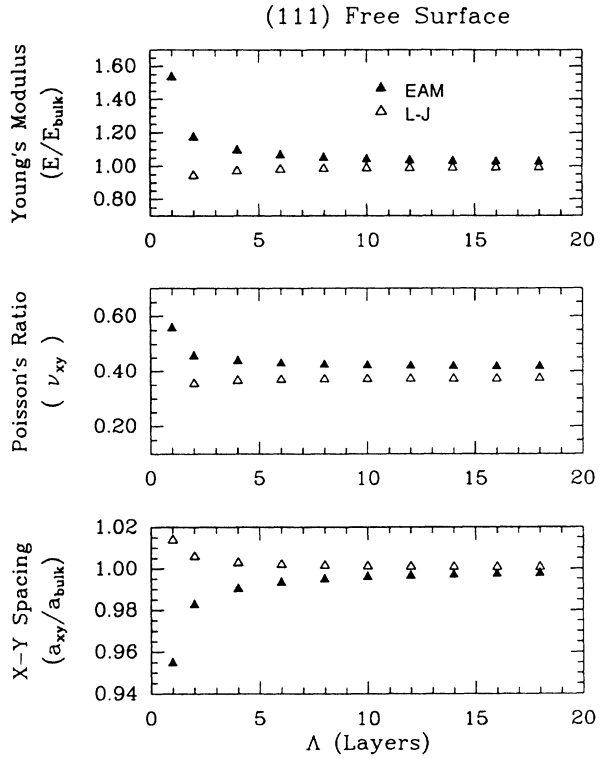

FIG. 2. Variation with film thickness of Young's modulus, Poisson's ratio, and lattice spacing in the plane for fcc films with a (111) orientation. The elastic constants have been normalized by their bulk values.

in the (111) planes. The accompanying strains cause the in-plane elastic moduli to increase in the manner discussed in the thermodynamic model.[13]

Wolf and Lutsko[9,14] have investigated the elastic properties of grain boundary superlattice structures as a function of the bilayer repeat length. They examined the behavior of $\Sigma 5(001)$ (twist) grain-boundary superlattices in the fcc structure using both LJ and EAM potentials. Their results on the alterations in lattice parameter and elastic properties are qualitatively similar to the results we obtained for (001)-oriented thin films. Consequently, they concluded that the elastic properties of grain boundary superlattices were equally well described by LJ and EAM potentials despite the obvious differences in the potentials. Our results for (111)-oriented fcc thin films indicate qualitative differences in the elastic behavior of LJ and EAM thin films and we suspect similar differences would occur for grain boundary superlattices composed of (111) boundaries.

In summary we report results on the elastic properties of fcc thin films. We find that in the (001) orientation the elastic properties of LJ and EAM films are governed by the intrinsic instability of these structures. Application of a pure shear causes the (001) open faces to transform to the more stable (111) face. The resulting structure is thermodynamically stable owing to a reduction in the surface energy of the film. This is the first report of such a transformation stabilized by finite-size effects. In the (111) orientation there are qualitative differences in the elastic behavior of LJ and EAM films as expected from the fundamental differences in the nature of these potentials. The results for the (111) EAM thin films are in reasonable quantitative accord with the thermodynamic model of Cammarata and Sieradzki.[13]

[1]D. Baral, J. B. Ketterson, and J. E. Hilliard, J. Appl. Phys. **57**, 1076 (1985).
[2]R. People and J. C. Bean, Appl. Phys. Lett. **47**, 332 (1985).
[3]R. People and J. C. Bean, Appl. Phys. Lett. **49**, 229 (1986).
[4]R. Danner, R. P. Huebner, C. S. L. Chun, M. Grimsditch, and I. K. Schuller, Phys. Rev. B **33**, 3696 (1986).
[5]A. Banerjea and J. R. Smith, Phys. Rev. B **35**, 5413 (1987).
[6]B. W. Dodson, Phys. Rev. B **37**, 772 (1988).
[7]Jan H. van der Merwe and W. A. Jesser, J. Phys. Appl. Phys. **63**, 1509 (1988).
[8]Jan H. van der Merwe and W. A. Jesser, J. Appl. Phys. **63**, 1928 (1988).
[9]D. Wolf and J. F. Lutsko, Phys. Rev. Lett. **60**, 1170 (1989).
[10]B. W. Dodson, Phys. Rev. Lett. **60**, 2288 (1989).
[11]B. M. Clemens and G. L. Eesley, Phys. Rev. Lett. **61**, 2356 (1989).
[12]M. L. Huberman and M. Grimsditch, Phys. Rev. Lett. **62**, 1403 (1989).
[13]R. C. Cammarata and K. Sieradzki, Phys. Rev. Lett. **62**, 2005 (1989).
[14]D. Wolf and J. F. Lutsko, J. Mater. Res. **4**, 1427 (1989).
[15]R. C. Cammarata and K. Sieradzki, Appl. Phys. Lett. **55**, 1197 (1989).
[16]G. J. Ackland and M. W. Finnis, Philos. Mag. A **54**, 301 (1986).
[17]M. I. Baskes (private communication).
[18]Raju P. Gupta, Phys. Rev. B **23**, 6265 (1981).
[19]R. Benedek, J. Phys. F **8**, 1119 (1978).
[20]R. A. Johnson, Phys. Rev. B **37**, 3924 (1988).
[21]M. Parrinello and A. Rahman, Phys. Rev. Lett. **45**, 1196 (1980).
[22]R. A. Johnson and P. J. White, Phys. Rev. B **13**, 5293 (1976).